

**Executive Summary** 

OFFICE OF NAVAL RESEARCH CARBON FIBER STUDY GROUP

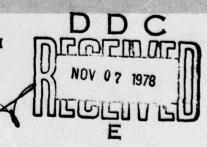
1 September 1978

Final Report

APPROVED FOR PUBLIC RELEASE; DISTRIBUTION UNLIMITED

Prepared for

OFFICE OF NAVAL RESEARCH
METALLURGY AND CERAMIC PROGRAM
Arlington, Virginia 22217



DDC FILE COPY

SECURITY CLASSIFICATION OF THIS PAGE (When Date store	READ INSTRUCTIONS
REPORT DOCUMENTATION PAGE	BEFORE COMPLETING F
FRØ39-16Ø-1	(9)
CARBON FIBER ELECTRICAL	. TYPETOF REPORT & PERIOD C
RESISTANCE MODIFICATION - ITS	Final rept
RELATIONSHIP TO ELECTRICAL EQUIPMENT	S DEPENDING ORG DEPORT H
MALFUNCTION. Executive Summary.	14) TR-0078(3721-11)-1
Office of Naval Research Carbon Fiber	CONTRACT OF GRANT NUMBER
Study Group	FØ4701-77-C-9078
9. PERFORMING ORGANIZATION NAME AND ADDRESS	10 BROGRAM EL EMENT BROJEC
The Aerospace Corporation	10. PROGRAM ÉLEMENT, PROJECT
El Segundo, Calif. 90245	
11. CONTROLLING OFFICE NAME AND ADDRESS	12. REPORT DATE
Office of Naval Research	1 September 378
Arlington, Virginia 22217	15
MONITORING AGENCY NAME & ADDRESS(If different from Controlling Office)	15. SECURITY CLASS. (of this repo
(2) 180	Unclassified
7 10p.	15a. DECLASSIFICATION DOWNGE
16. DISTRIBUTION STATEMENT (of this Report)	SCHEDULE
Approved for public release; distribution unlimit	
Approved for public release; distribution unlimit	ed
Approved for public release; distribution unlimit	ed
Approved for public release; distribution unlimit  W.T. Barry  R. J. Diefendorf	ed
Approved for public release; distribution unlimit  W.T. Barry  R. J. Diefendorf  Bupplementary notes  M. S. Dresselhaus	om Report)  D D C
Approved for public release; distribution unlimit  W.T. Barry  R. J. Diefendorf	om Report)
Approved for public release; distribution unlimit  W.T. Barry  R. J. Diefendorf  Bupplementary notes  M. S. Dresselhaus	om Report)  D D C
Approved for public release; distribution unlimit  DISTRIBUTION OF TEMBER (OF the abstract entered in Block 2011 different for  W.T. Barry  R. J. Diefendorf  18. Supplementary notes  N. S. Dresselhaus  R. I. Gray  M. F. Hawthorne  19. Net WORDS (Confines an arrange side if necessary and identify by block number	NOV 0 7 1978
Approved for public release; distribution unlimit  DISTRIBUTION OF TEMENT (OF the abetract entered in Block 2011 different for  W.T. Barbay  R. J. Diefendorf  18. Supplementary notes  R. J. Gray  M. F. Hawthorne  19. Net WORDS (Continues on source side it message)  Carbon Fibers  Fire	NOV 0 7 1978
Approved for public release; distribution unlimit  DISTRIBUTION OF TEMENT (OF the abeliaci entered in Block 2011 different for  W.T. Barby  R. J. Dieferschaus  18. Supplementary notes  N. S. Dresselhaus  R. I. Gray  M. F. Hawthorne  19. Rev NORDS (Continue of the little of the block number  Carbon Fibers  Electrical Equipment  Electrical Resistivity	NOV 0 7 1978
Approved for public release; distribution unlimit  ONT. Barry  R. J. Diefendorf  18. Supplementary notes  N. S. Dresselhaus  R. I. Gray  M. F. Hawthorne  Carbon Fibers  Electrical Equipment  Explosion	NOV 0 7 1978
Approved for public release; distribution unlimit  Description of the many of the shelfect entered in Block 2011 different for  W.T. Barry  R. J. Diefer and the many of the m	nov 07 1978
Approved for public release; distribution unlimit  Distribution extrement for the abstract entered in Block 20, if different to  W.T. Barby  R. J. Diefer Laus  N. S. Diefer Laus  R. L. Gray  M. F. Haw thorne  19. Net WORDS (Confines an entered in necessary and identify by block number)  Electrical Equipment  Electrical Resistivity  Carbon-Carbon Composites  10. ABSTRACT (Continue on reverse side it necessary and identify by block number)  A problem exists in the operation of electrical e	nov 07 1978
Approved for public release; distribution unlimit  Description of the many of the shelfect entered in Block 2011 different for  W.T. Barry  R. J. Diefer and the many of the m	nov 07 1978  quipment if carbon fibe when accidentally dis-

DD FORM 1473

999500 SECURITY CLASSIFICATION OF THIS PAGE (When Date En

SECURITY CLASSIFICATION OF THIS PAGE(When Date Entered)

19. KEY WORDS (Continued)

20. ABSTRACT (Continued)

Fiber Study Group was convened to consider whether or not the electrical resistance of carbon fibers could be increased to acceptable levels without altering other desirable characteristics. The group considered (1) the magnitude of resistance changes required to minimize electrical equipment malfunction, (2) whether or not carbon fibers can be modified to meet these requirements, (3) the ease of hardening confined spaces, and (4) the disposal of carbon fibers and composites after use. Conclusions, recommendations, and background information are presented herein.

#### PREFACE

The work described in this report is the result of the contributions of the following members of The Office of Naval Research Fiber Study Group:

> W. T. Barry The Aerospace Corporation, El Segundo, California

R. J. Diefendorf Rensselaer Polytechnic Institute, Troy, New York

M. S. Dresselhaus Massachusetts Institute of Technology, Cambridge, Massachusetts

R. I. Gray Naval Surface Weapons Center, Dahlgren, Virginia

M. F. Hawthorne University of California, Los Angeles, California

A. J. Heeger University of Pennsylvania, Philadelphia, Pennsylvania

R. A. Meyer, Chairman The Aerospace Corporation, El Segundo, California

L. H. Peebles, Jr. Office of Naval Research, Boston, Massachusetts

D. M. Riggs Army Materials and Mechanics Research Center Watertown, Massachusetts

W. P. Slichter Bell Telephone Laboratories, Inc., Murray Hill, New Jersey

The Office of Naval Research Fiber Study Group acknowledges and expresses appreciation for the very helpful assistance provided us through the sharing of information by persons from the following organizations:

Army Ballistic Research Laboratory, Aberdeen, Maryland D. J. Hinz Dr. K. A. Pullen Dr. L. J. Vande Kieft

Ford Motor Company, Detroit, Michigan Dr. J. J. Harwood

Great Lakes Research Corporation, Elizabethton, Tennessee Dr. L. A. Joo R. Prescott

McDonnell Douglas Astronautics Company Huntington Beach, California A. J. Cwiertny

NASA Langley Research Center, Hampton, Virginia D. L. Dicus Washington, D.C., Headquarters D. P. Williams III

Naval Research Laboratory, Washington, D.C. Dr. V. R. Deitz

Dr. R. L. Jarvis Dr. J. P. Reardon

Naval Surface Weapons Center, Dahlgren, Virginia

Dr. R. A. Amadori

L. C. Copen C. E. Gallaher R. L. Hudson D. L. Marker

Dr. K. A. Musselman Dr. V. G. Puglielli

Dr. R. E. Richardson

Stackpole Fibers, Lowell, Massachusetts

P. G. Boyd G. G. Fleming G. F. Pauline

Union Carbide Corporation, Parma, Ohio J. H. McFerrin

New York, New York
Dr. W. E. Chambers

J. R. Paus H. N. Townsend

# CONTENTS

PRE	CFACE		1
ı.	INT	RODUCTION	5
II.	CON	CLUSIONS AND RECOMMENDATIONS	7
	Α.	Conclusions	7
	в.	Recommendations	10
	c.	Discussion of Recommendations	11

## I. INTRODUCTION

Individual carbon fiber filaments can be released from carbon-fiber reinforced composites when the latter are subjected to severe environmental conditions such as fire, explosion, impact, and wear. The highly electrically conductive fibers, so released, can interact with electrical equipment and cause their malfunction by such phenomena as short circuits, arcs. and coronas.

Because of the potential for increased use of carbon fibers for aerospace and automotive applications and for a variety of consumer products, the changes of contamination by airborne fiber are also increasing. Furthermore, because the fibers are stiff, strong, and have low density, they are used in composites to reduce weight, which is an important factor in conserving energy. Industries have already committed large capital expenditures for material development and are planning further expansions for production provided that the potential threat of airborne fibers can be controlled.

A Carbon Fiber Study Group was convened by the Office of Naval Research (ONR) to consider whether or not the fiber resistance of carbon fiber could be increased sufficiently to minimize the hazards to electrical equipment. The group considered whether or not the modifications to the fiber resistance could be accomplished without undue sacrifice to the modulus and strength.

The objective of the study was to define research approaches that might alleviate the potential problems. The conclusions and recommendations are based on discussions with experts in fiber manufacturing, fiber utilization, and the influence of fibers on electrical equipment malfunctions. The effects of variations in the composition and morphology of the fiber on the electrical resistance and mechanical properties were also considered. The conclusions were made largely on the basis of unpublished information and on analyses performed by committee members.



The results of the study are published as two separate reports: The Executive Summary, 039-160-1 (TR-0078(3721-11)-1), and The Executive Summary combined with background information, 039-160-2 (TR-0078(3721-11)-2).

#### II. CONCLUSIONS AND RECOMMENDATIONS

# A. CONCLUSIONS

The extent of the problem of carbon fiber release as a hazard to the operation of electrical equipment and its relationship to major disruptions has not been fully evaluated and indeed may be overstated. The severity of the hazards needs to be ascertained by means of a risk analysis with appropriate experimental data.

It is technically feasible and routine in most industrial plants, particularly those involved in the production and handling of carbon fibers, to protect electrical equipment against carbon fiber intrusion. The balance between the cost of protection and the potential hazard must be evaluated for each situation. A combination of awareness of the problem, good housekeeping, hardening of equipment, and reduction of the release of highly conducting fibers will reduce the hazard to acceptable levels relative to the benefits to be derived from the use of carbon-fiber-reinforced plastics and resins.

Analysis of the breakdown of electrical circuits indicates that three voltage ranges might be considered: low (less than 18 V), medium (18 to 500 V), and high (greater than 500 V). In the high-voltage regime, the high conductivity of carbon fibers does not present any additional hazards other than those already experienced by other high-voltage pollutants such as sea or road salt, cement dust, and bird droppings.

Hazards in all voltage regimes can be reduced by several methods, for example, the prevention of accidental dispersion of fibers by containment,

<sup>\*&</sup>quot;Carbon Fiber Study," NASA Technical Memorandum 78-718 (May 1978).

the use of nonflammable matrices in composites, and the catalysis of low-temperature oxidation of fibers. In the low and medium voltage regimes, coating the fibers with an insulating material or increasing the resistance of the fibers can also reduce the hazards. In theory, it is possible to increase the settling rate of dispersed fibers by increasing the diameter; in practice, only small increases in diameter and hence settling rates can be achieved.

A serious problem might arise in disposing of scrap, broken, or obsolete parts. This problem may exceed that generated by accidental release in service. The burning of junked items under uncontrolled conditions is a principal cause for concern.

There are no "quick-fix" solutions for reducing or eliminating the potential hazard occasioned by dispersed carbon fibers by modifying the materials used in composites. Any such modifications will require, at best, several years for development, evaluation, and requalification before the composite can be certified for use.

In the low voltage regime (≤18 V) an important parameter is the contact resistance and associated punch-through phenomenon in addition to fiber bulk resistance. Punch-through, the penetration of surface barrier films by the fibers, can occur at about 2 V. Surface resistances greater than 10<sup>6</sup> ohm/cm would significantly reduce the hazard for single-fiber bridgings.

No general conclusions can be made concerning fiber resistance requirements independent of circuit impedance to minimize the problem in the medium voltage regime (18 to 500 V) because of the many diverse applications involved. However, preliminary studies indicate that bulk resistances greater than 10<sup>6</sup> or 10<sup>7</sup> ohm/cm significantly reduce the probability of arc initiation, and resistances greater than 10<sup>4</sup> ohm/cm reduce the danger of shock to personnel.

Fiber resistance is considered to play an important part in causing equipment failure. Typical commercial fiber resistances range from 90 to 15,000 ohm/cm with many near 2000 to 8000 ohm/cm.

Current evidence indicates that resistances of about  $10^6$  ohm/cm can probably be attained. Polyacrylonitrile (PAN)-base carbon fibers can now be produced with 4.07 GPa ( $30 \times 10^6$  psi) modulus, 2.07 GPA ( $300 \times 10^3$  psi) tensile strength, and  $2 \times 10^5$  ohm/cm by retaining appreciable nitrogen. The extent of improvement that can be obtained and the effects of fire on the fiber resistance is not yet certain. Further research is required.

The preparation of intercalation compounds from carbon fibers to increase the electrical resistivity while maintaining the high modulus offers little potential for reducing the airborne fiber hazard. The use of intercalation processes to prepare stable materials with high resistivities may, however, be possible. Because many materials intercalated or otherwise placed into carbon fibers tend to be unstable, composite aging problems and the degradation of interfacial bonding may result.

Examination of available resistivity-modulus-strength data for various fiber types indicates that the PAN-base fibers appear to offer the most promising compromise for ameliorating the airborne fiber problem. The available pitch fibers are much more conducting at equivalent moduli. However, because research on increasing the resistance of pitch-type fibers is not as advanced as that on PAN-base fibers, these should not be eliminated from consideration as alternative fibers for the airborne fiber problem.

A low-temperature processing approach appears to have merit in increasing resistance because of the retention of foreign atoms and increased disorder of the crystallites in both PAN- and pitch-base fibers. However, it has not been established whether or not acceptable fiber mechanical properties can also be maintained by this method.

The application of a coating to fibers appears to be a promising approach for either increasing the surface resistance or preventing dispersal of free-flying fibers. Care must be taken to ensure that the desirable properties of the fiber or the adjacent matrix are not degraded.

Insufficient information exists about the electrical and mechanical properties as well as the surface and bulk morphology of fibers released from multicomponent composites after exposure to different types of severe

environments such as impact and fire or explosion or both. Such information is necessary for risk analysis calculations in order to evaluate more accurately the effectiveness of any proposed material modifications.

# B. RECOMMENDATIONS

The recommendations given here are not ranked by priority within each category.

#### 1. GENERAL CONSIDERATIONS

- a. Risk analysis must be expanded to include all current and potential major applications. Sources for the utilization of fibers considered should include automotive and industrial applications, sporting goods, and aerospace applications. Consideration should be given to release mechanisms of fiber other than by burning or explosion or both, e.g., wear-erosion of carbon-carbon brakes.
- b. In order to prevent duplication of efforts, an information and coordination system should be established among those organizations concerned with the problem of airborne carbon fibers.
- c. Information on the potential hazards in the use and disposal of carbon fibers should be communicated to the users of carbon fibers by the manufacturer.
- d. Methods should be developed and evaluated for the disposal of carbon fiber in a manner that is safe now and in the future.

### 2. SPECIFIC RESEARCH APPROACHES

- a. Work should be carried out on matrix systems to minimize fiber dispersal. The objective would be to limit the dispersion of fibers by providing better fiber/matrix bonding and higher char yield to hold fibers together. Char on the fiber may also enhance its surface resistance. Consideration should also be given to the development of special matrices to enhance the oxidation of the fibers when exposed to fire.
- b. The retention of nitrogen in the PAN-base carbon fibers has been shown to yield increased resistance. The extent to which resistance can be increased without sacrifice of mechanical properties should be examined.

- c. Because nitrogen retention yields increased resistance, other foreign atoms should be considered for incorporation into the carbon structure in order to obtain desired properties.
- d. More intensive work should be directed toward the coupling of mechanical, electrical, and morphological properties of the fibers. Most studies have concentrated on either the combined mechanical-morphological or the electrical-morphological properties but not on the coupled interactions. The coupled interactions should also be studied in cases where intercalation processes result in stable carbon compounds.
- e. Alteration of various processing conditions prior to heat treatment, including precursor modifications, fiber spinning, and stabilization conditions should be undertaken for both PAN and pitch precursors in order to optimize fiber properties.
- f. The application of coatings to fibers that form either insulating chars or high-resistance fibers on exposure to fires should be investigated. A promising coating system appears to be based on a carborane-siloxane system.
- g. Detailed evaluations should be made of the fibers that are released from composites that have been exposed to environmental conditions such as impact and fire. These evaluations should include values of surface and bulk electrical conductivity, morphology, and in particular their surface conditions. This information would be used in risk analysis for determining the probability for disabling equipment. Particular attention should be given to investigation of the condition of the fibers after the incident.

## C. DISCUSSION OF RECOMMENDATIONS

The paragraphs presented here are keyed to the corresponding recommendation presented in the preceding section.

(1a) The risk analyses thate are now available and in preparation are mostly concerned with the application of carbon fiber technology to aircraft and aerospace vehicles. Carbon fibers may well find wide use in the automotive industry and are being used in other civilian-oriented markets such as sporting goods and industrial equipment. Consequently, risk analyses should be expanded to include the manufacture, use, and planned or accidental

destruction of such items as automobiles and tennis rackets. The use of carbon-fiber-containing products by the military is subject, in principle, to tight control of use and disposal. This control is not available for the use and disposal of carbon fiber products by the population at large. Misguided or negligent manipulation of carbon fibers could result in serious problems. A survey should be made and kept current to identify other potential and actual uses of fibers and the risks involved in their application. Continuous use of carbon fiber products will also result in the dispersal of fibers by wear and erosion mechanisms. An example is carbon fiber aircraft brakes, which, under use, may emit a fine powder of carbon. Clearly, this and other mechanisms for dispersal must be examined and included in the analysis.

- (lb) In order to prevent duplication of efforts, an information exchange and task coordination system should be established. At a recent meeting held by NASA, 52 companies, 8 universities, and 22 government installations were present and reported involvement in various aspects of the carbon fiber problem. This roster of interested and involved organizations will undoubtedly continue to expand, and the generation of new concepts, analyses, and materials will expand accordingly. Coordination of this information flow is essential for the expeditious development of the overall program and awareness by the public use and potential hazards of carbon fibers. A leading organization in the field of carbon fiber technology should take responsibility for the dissemination of information.
- (1c) The many users of fibers with diverse end-item application must be made aware of the risks to electrical equipment. Only a few manufacturers include a "potential hazard" label on packages of

carbon fibers. More awareness of the risks should be noted by including detailed instruction for proper disposal on all fiber packages shipped to customers. Some consideration should be given to the larger question of whether or not all carbon fiber products should contain warning labels concerning their proper disposal.

- (1d) Methods for the disposal of carbon fibers present a problem because of their resistance to oxidation and the ease with which they can be dispersed in the air. A common method of disposal is to bury plastic bags of fibers in a controlled land fill. No information is available about the subsequent degradation or potential dispersal within such sites. Other methods of disposing of fibers and parts containing fibers should be investigated before the problem becomes acute or extremely expensive or both because of the lack of proper containment.
- (2a) Carbon fibers are released from composite matrices by failure of the fiber matrix bond on impact and explosion or by the preferential combustion of the matrix in a fire. Consequently, desirable matrices would be those impact-resistant materials that give the required structural properties of the system coupled with enhanced or tumescent char yields during combustion. The preferential combustion of matrices could be mitigated by the synthesis of polymers that have good fiber coupling and fire-retardant properties and produce a tumescent char during combustion. It is well within the present state of polymer science to approach these problems with some assurance of success, and such efforts of this sort should be emphasized.
- (2b) It has been noted that PAN-base fibers processed at low temperatures to give reasonable strength and modulus values also give higher resistance. Further research and development are

necessary in order to determine the limits of the method for optimizing the resistance versus the mechanical properties of these fibers.

- (2c) If the improved resistance of PAN-base fibers is a direct result of nitrogen retention, other types of additives should be investigated to determine if they can be incorporated into the carbon fiber structure in order to increase resistance while retaining suitable mechanical properties and matrix adhesion. Additives that are stable at high processing temperatures and can withstand exposure to fire would be highly desirable.
- (2d) In order to obtain optimum fiber properties, a somewhat disordered microstructure may be desired. Highly conducting carbons have a very highly ordered carbon microstructure. Studies on the electrical characteristics of carbon fibers have usually been carried out with the use of commercially produced materials. There is very little data available on the influence of processing conditions on both mechanical and electrical properties. Such studies should be undertaken.
- (2e) More sophisticated uses of carbon fibers may require physical properties than can only be attained from one of the precursor fibers. For example, there are certain applications for the military where a modulus near 683 GPa (100 × 10 psi) is required. This value indicates consideration of a pitch-rather than a PAN-base fiber. In contrast, PAN-base fibers can be produced with a higher electrical resistance and still retain a higher modulus value as compared to a pitch-base fiber. Consequently, no class of fibers should be eliminated and considered unsatisfactory. Rather, tradeoffs may have to be made and more knowledge obtained about the interactions between properties. In considering these precursors, practically no effort has been made to

modify the composition or structure or both of the precursor materials used in PAN- or pitch-base fibers to enhance resistance yet retain good mechanical properties of the resulting carbon fibers. Furthermore, if low-temperature processing is the correct method of increasing fiber resistance, modifications in the as-spun fiber structure should have marked effects on the ultimate carbon fiber properties. Many carbon fibers have a highly ordered, conductive skin with a less-ordered, less-conductive core. Adjustments in the fiber formation and fiber stabilization processes may alter the fiberial structure and skin-core gradients and yield improved overall properties. There is little published evidence available on how the fiber formation and the stabilization processes influence subsequent processing and properties of carbon fibers. Little effort has been directed toward determining the influence of processing conditions, morphological changes, and intercalation on the combined mechanical and electrical properties of carbon fibers. Such studies should be encouraged.

(2f) Coating the fibers with a highly insulative layer is one way to reduce the electrical hazard. The insulation can be obtained by using coating materials such as oxides and carbides or with chars that have high resistance or become low-density foams that spatially insulate the fiber. Other types of coatings might be beneficial, such as polymeric materials that thermally decompose to produce a char or residue capable of holding fibers together and provide electrical insulation. Polymetric coatings may also be effective for landfill disposal. Any coating selected should be tested to determine its effect on composite properties and whether or not it remains effective after dispersion.

The effectiveness of carbon fibers in causing the disruption of electrical equipment depends on their bulk and surface resistance. Furthermore, the properties of fibers expelled from the composite may differ significantly from the morphological, electrical and mechanical characteristics of the original fibers. Studies should therefore be undertaken to determine these characteristics.

Such information will be particularly useful in the risk analysis. Methods for characterization must be carefully selected in order to preserve the post-environmental test character of the fibers.